

## INTEGRATED TWO-STAGE LIQUEFACTION: THE LEGACY AND THE UNFINISHED WORK

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### INTRODUCTION

The Integrated Two-Stage Liquefaction (ITSL) concept has received considerable attention by many laboratories and has emerged as one of the most promising technology in direct coal liquefaction.

DOE/Lummus/Cities Service, EPRI/Kerr McGee, the Wilsonville teams, Chevron and Exxon (1) have been in one way or another involved in processes conforming to the ITSL concept, each one with a somewhat different approach or processing scheme. Recently, HRI (2) has developed another staged liquefaction concept which recently has received DOE support for extended continuous bench-scale testing.

Major achievements were obtained during the development of the ITSL process at Lummus, from May 1980 to June 1985, which have changed substantially our approach to coal liquefaction techniques and inspired new thoughts in unraveling the mechanism of direct coal liquefaction at low severity operations. These novel mechanistic considerations need to be supported with further studies using suitable model compounds, some of which have been recently proposed (3).

Several papers have reported the early development of the ITSL process and related projects (4-8). This paper has the objective to divulge the most recent achievements of an evolved ITSL process, pointing out the unfinished work, and to expand the concept of the low-severity staged approach which resulted from the evolved ITSL process and emerged as the most desirable pathway for the direct production of marketable liquid fuels from coals. The ultimate objective is to interest the researchers dedicated to fundamentals of coal liquefaction toward the technological needs and the understanding of reaction mechanism, kinetics and thermodynamic limitations residing with the novel, low-severity staged coal liquefaction approach.

### THE ITSL LEGACY

Major accomplishments obtained at low-severity operations in a 3/4 ton/day ITSL process development unit at Lummus and from related bench-scale studies in various laboratories, include:

Low severity produced extracts are low in heteroatoms and more easily hydrogenatable, consistently yielding excellent equilibrium donor solvent (9).

No high viscosity gel region is apparent over the 280-350°C temperature range for a slurry of bituminous coal and ITSL solvent, as was the case for slurries prepared with the same coal and other types of solvent (10).

Low severity processing forms mostly reactive low molecular-weight fragments. Conversely, single stage thermal and thermal/catalytic processing produce high-molecular weight products thought to be actually condensation products of such smaller fragments and consequently, less reactive (11).

Proton NMR analysis, modified to provide data on ITSL distillate and non-distillate fractions, has been shown to be useful in the development of a kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation and cracking reactions, and to predict the solvent donor capability as well as the yield structure of the upgraded products (12).

A mixture of condensed aromatics, hydroaromatics, paraffins and their respective heteroatom derivatives is produced during coal liquefaction. This mixture tends to be unstable because of the incompatibility between polar heteroatom compounds and hydrocarbons, as well as between condensed aromatics and paraffins. Condensed hydroaromatics, having closer affinity for both aromatics and paraffins, tend to keep them in solution, thus contributing to the stability of the coal extract. Low severity coal extraction yields a larger quantity of hydroaromatics and small amounts of high heteroatom, condensed aromatics and paraffins (12).

Best catalysts tested are those modified to suppress the hydrocracking activity and enhance hydrogenation functionality (9).

Coal derived transportation fuels, produced by refining of distillate from low severity operations, possess inherent high quality which is due mostly to their hydroaromatic (naphthenic) nature. Coal derived naphthas contain large quantities of highly alkylated cyclohexanes which, by reforming, convert to the corresponding benzenes and in the process, recover a large portion of the hydrogen to make the overall coal liquefaction approach economically more attractive. Alkylated benzenes are the major contributors to the high octane gasoline thus formed. Coal derived middle distillate is constituted mostly of di- and tri-hydroaromatics and corresponding aromatics.

Further refining has been successfully employed to convert some of the aromatics to meet marketable jet and diesel specifications of smoke point and cetane number, respectively (13).

From the operation of the process development unit (PDU) at Lummus (9) the following important results were obtained:

Subbituminous coal was demonstrated to be an attractive feed for direct liquefaction: The distillate yield was slightly lower (2.9 bbl/ton of moisture-ash-free coal compared to 3.2 for bituminous coals) but its lower cost, higher reactivity in the second stage and its ease in being converted to a lighter product

are over-riding features in its favor. In addition, ITSL with Wyodak coal demonstrated good operability in both reaction stages and was easily deashed.

When the deasher is placed after the LC-Fining reactor, the distillate yield was increased seven percent. More importantly, the LC-Fining catalyst was unaffected by ash feed and reactor volume is unchanged.

Most of the LC-Fining reactor volume could be replaced by a fixed bed hydrocracking unit. This resulted in an equally good yield of -650°F product with no loss in hydrogen efficiency. The -650°F product contained less than 100 ppm sulfur and less than 500 ppm nitrogen, making this a clean, light and environmentally acceptable product. Furthermore, this flow configuration reduces the second stage reactor volume by at least 18 percent and may also greatly simplify and reduce the cost of the deashing section.

The SCT reaction was operated at 500 and 1000 psig, with no adverse effect on yields or hydrogen usage. This leaves the LC-Fining as the only high pressure section of the process.

Analysis of the results indicated that a commercial SCT reactor can be designed to retain all the important features of the PDU. There is every reason to believe that SCT can be scaled to commercial size.

Deasher bottoms were coked to produce additional liquid products. The liquid yield was about 20 percent of the organic matter in the ash-rich feed.

Low temperatures of about 700°F, do not provide sufficient hydrogenation to replenish solvent quality, while at 800°F the solvent contains insufficient transferable hydrogen. Therefore, the optimum temperature for both conversion and regeneration of recycle solvent is about 724-750°F (9).

In antisolvent deashing experiments, THF-insoluble/quinoline-soluble preasphaltenes precipitate consistently with the mineral matters, whereas the THF-soluble preasphaltenes do not. This indicates that THF-insoluble preasphaltenes may be the major cause of mineral matters agglomeration, increasing their diameter and causing the particles to settle faster (14).

#### THE UNFINISHED WORK

The most significant achievements of the ITSL program came into focus during the last part of the ITSL project and of the related projects before they ceased operation. In this particular period, those who closely monitored the overall program, gathered the large set of data made available, and structured them for suitable process engineering and economic evaluation,

became aware of an evolutionary trend in coal liquefaction processing. The major factors contributing to this novel trend were: 1) the better understanding of the very sensitive interdependency between the stages of coal extraction, of the coal extract upgrading and hydrogen donor recycle solvent requirements, which emerged only from the data produced in a continuous, integrated recycle mode of operations, and 2) the more favorable results of low-severity operations, practically solving, in an easy and elegant manner, most if not all the problems encountered by using high-severity operations which were practiced in earlier processes, i.e. German, H-Coal, SRC-II, etc.

But perhaps more important to the fundamental research community is the fact that the large set of ITSL data under scrutiny for process development, lacks the fundamental data to support the profound changes in the mechanism and kinetics occurring at low-severity coal liquefaction.

Some of the concepts and technology needs are outlined below.

Preservation of highly reactive, small fragments in the coal extract is of utmost importance in producing an excellent donor solvent and high quality distillate fuel products. For this purpose, the fragments should be withdrawn from the extraction reactor as soon as they are formed. The unconverted coal can be further converted by recycling it with the preasphaltenes as part of the recycle solvent.

Better preservation of the reactive small fragments can be achieved by increasing the donatable hydrogen level and decreasing the heteroatom content of the recycle solvent. It is important for the superior hydrogen donor solvent to penetrate the less reactive macerals. Consequently, it is advisable to allow for a thermal soaking treatment, i.e., at 250-350°C temperature range for 10-30 minutes, prior to the short contact time (SCT) reaction of rapid heating (two minutes) to the 450°C exit temperature. It is evident that all the above activities are interdependent and the improvements maximized in an integrated recycle process.

It is extremely difficult to capture in research bench scale units the essence of the results produced in the integrated recycle process, because most of the key benefits, i.e., coal conversion and enhanced donor solvent quality, are obtained only after several cycles of the integrated staged operations. Bench scale researchers could avoid the long and tedious recycle operations by applying the aforementioned kinetic model for coal extract hydroprocessing (12) and using proton-NMR data of the coal extract to predict solvent donor capability and yield structure of the upgraded products.

Proton-NMR analysis is rapid, requires small samples, is highly reliable and has excellent reproducibility.

Removal of the heteroatoms in the early stage of coal extraction is desirable and ought to be sequential, removing first the more abundant oxygen and thus making easier the subsequent nitrogen removal.

Complementary fundamental studies on C-O and C-N bond scission should be emphasized over the current C-C bond cracking effort.

Most of the sulfur is converted to hydrogen sulfide during the two above sequences, and the  $H_2S$  must be kept in the system as catalyst itself and as "activator" of transition metal catalysts.

It is essential that the ITSL technology be pursued to the completion of the evolutionary trend which became almost dormant with the termination of most of the ITSL projects. It is up to the fundamental research community to fill-up the gap of supportive fundamental research through studies of thermodynamics, kinetics and reaction mechanisms involved in low-severity operations which are part of the ITSL process. Of particular interest would be the matching of reaction kinetics of dehydrogenation of the hydrogen donor solvent with the hydrogen acceptancy of coal extracts.

Those of us involved in these efforts are optimistic about the future of low-severity direct coal liquefaction and the quite similar coal/oil co-processing as the practical approaches in helping to alleviate an increasingly energy-deficient world.

#### REFERENCES

1. S. Zaczepinski, Exxon ER&E Co., Private communication, April 1983.
2. A.G. Comolli, E. J. Hippo and E. S. Johanson, "Two-Stage Direct Liquefaction," McGraw-Hill Science and Technology of Synfuels II, New York City, NY, February 2-4, 1983.
3. E. C. Moroni, F. B. Burke, R. A. Winschel and B. W. Wilson, "Integrated Two-Stage Liquefaction Process--Solvent Quality Effects," ACS National Meeting, Seattle, WA, March 20-25, 1983.
4. M. Peluso, A. N. Schiffer and H. D. Schindler, "The Two-Stage Liquefaction Process (ITSL)." Coal Technology '81 Meeting, Houston, Texas, November 1981.
5. H. D. Schindler, J. M. Chen, M. Peluso, E. C. Moroni and J. D. Potts, "The Integrated Two-Stage Liquefaction Process (ITSL)," AIChE Annual Meeting, New Orleans, LA, November 1981.
6. M. B. Neuworth, "Advanced in Two-Stage Liquefaction" 9th Energy Technology Conference, Washington, D.C., March 1982.
7. E. C. Moroni, "Future Development for the ITSL Concept," 7th Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, CA, May 11-13, 1983.
8. M. B. Neuworth and E. C. Moroni, "Development of an Integrated Two-Stage Coal Liquefaction Process," Fuel Processing Technology, 8, (1984) 231-239, Elsevier Science Publishers.

9. H. D. Schindler, J. M. Chen and J. D. Potts, "Integrated Two-Stage Liquefaction", Final Technical Report - DOE Contract No. PC 50021-Q11, July 1985.
10. B. R. Rodgers, Oak Ridge National Laboratory, Private Communication, 1983.
11. J. H. Shinn, "From Coal Single-Stage and Two-Stage Products: A Reactive Model of Coal Structure," Fuel, Vol. 63, 1187, 1984.
12. J. M. Chen and H. D. Schindler, "A Lumped Kinetic Model for Hydroprocessing Coal Extract," AIChE Spring National Meeting, Houston, TX, April 1985.
13. R. F. Sullivan, "Two-Stage Hydrocracking of ITSL Oil for Jet Fuel and Naphtha," Proceedings of Direct Coal Liquefaction Contractors' Review Meeting, Albuquerque, NM, Page 238, October 1984.
14. R. A. Winschel and F. P. Burke, "Recycle Slurry Oil Characterization" Second Annual Report, October 1, 1981 through September 30, 1982, DOE Contract PC 30027-39, August 1983.